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Determination of Hf, Sc and Y in geological samples together with the rare-earth elements

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Abstract A method is described for the determination of Hf, Sc and Y simultaneously with the REE in geological materials. An earlier method for REE separation from major elements was studied with the aim to apply it also to the determination of Hf, Sc and Y. Sample decomposition was carried out by melting with $LiBO_2$. The method involves separation and concentration stages, using the cation-exchange resin DOWEX AG 50W-X8. Matrix elements were eluted with 2 mol/l HCl, whereas 6 mol/l HNO_3 with oxalic acid and 8 mol/l HNO_3 were used to elute the elements to be determined. Some of the matrix elements could not be completely removed. This effect as well as the recovery rates of the determined elements were investigated. The measurements were performed by ICP-AES. Spectral interferences were also tested.

Introduction

The determination of Hf, Sc and Y contents in geological materials has received considerable attention in recent years because of their importance for characterising magma sources. These elements are usually determined by X-ray fluorescence (XRF), instrumental neutron activation analysis (INAA) and more recently by ICP-AES [1, 2]. However, the low contents of these elements in rocks and minerals, as well as the strong interferences from matrix elements, require separation and concentration stages prior to the quantitation of the elements by ICP-AES. The separation methods are the same as those used for the rare-earth elements (REE), which are accompanied by Hf, Sc and Y. Very often these methods are based on the separation with cation-exchange resins. A detailed review and comments on the methods of separation and determination are given in [3, 4]. A method for the determination of Y with the REE group is described in [4–7], of Sc in [3, 4, 8] and of Hf, Sc, Y in [4].

This paper describes a method for the determination of Hf, Sc and Y, based on the procedure given by [9] for the determination of REE. This procedure is currently used for the determination of REE also at the chemistry laboratory of our department. In order to determine Hf, Sc and Y in addition to and together with these elements, we added an elution step in the presence of oxalic acid [4].

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Experimental

All chemicals were of analytical reagent grade, supplied from Fluka. Hf, Sc and Y standards were 1 g l^{-1} stock solutions from Johnson and Matthey. Working solutions were obtained by suitable dilution with 5% nitric acid. For decomposition 0.5000 g of sample was thoroughly mixed with 1.50 g of lithium metaborate ($LiBO_2$) in a platinum crucible and then melted in a muffle furnace for 30 min at 1000 °C. The melt was cooled in an ultrasonic water bath. The bead thus prepared was placed in a glass beaker and dissolved by adding 50 ml 1.75 mol/l hydrochloric acid under stirring. The separation and concentration of REE and Hf, Sc and Y was carried out by means of the cation-exchange resin Dowex 50W-X8 100-200 mesh (in a column of 10 mm i.d., 20 cm length) converted to its H^+ form by equilibration with 100 ml 1.75 mol/l HCl. After loading the sample onto the column, the resin was first eluted with 100 ml 2 mol/l HCl and the eluates were discarded. Then the REE, Hf, Sc and Y were eluted with 50 ml of 6 mol/l nitric acid containing 0.005 mol/l oxalic acid, followed by 8 mol/l nitric acid. The eluates were collected in a 250 ml beaker and evaporated to 2–3 ml. The residue was transferred into a 25 ml beaker with 5% HNO_3 and again evaporated to dryness.

Prior to the ICP-AES measurements the residue was dissolved in 5% HNO_3 and passed quantitatively into a 10 ml graduated flask.

The measurements were made by means of a Perkin-Elmer Plasma 1000 spectrometer. The following operating parameters were used: instrument power 1 kW, plasma gas flow rate 15 l min^{-1}, auxiliary gas flow 0.3 l min^{-1}, carrier gas flow 1 l min^{-1}, sample uptake rate 2 ml min^{-1}, viewing height 15 mm above coil.

The following wavelengths were used: Hf 277.336 nm, Sc 361.384 nm and Y 371.030 nm. These wavelengths were selected after careful examination with the aim to obtain high sensitivity and remove spectral interferences. [4]

Results and discussion

It has been reported [4, 5, 10] that the REE, Hf, Sc and Y are often contained in minerals like zircon, which are highly resistant to acid decomposition. That is why the decomposition is accomplished by melting with $LiBO_2$ or by a combined procedure involving acid treatment and subsequent melting of the undissolved residue. We used the fusion with $LiBO_2$ which considerably simplifies the procedure of decomposition. The following separation step leads to a decrease of the high concentration of the melting agent.

Crock and al. [6] reported that early elution of Sc is possible Although this was not verified in later studies, we investigated the behaviour of Sc, Hf and Y because of the higher concentration of HCl (2 mol/l) used for the elution of the matrix elements. The contents of these elements were determined in 10 ml fractions collected during adsorption and elution. Neither early elution nor a loss of these elements was found. The recovery values were 98–99%.

One of the main reasons to utilize a two-step elution of the matrix elements with HCl and HNO_3 is the complete removal of Ca, Sr and Ba due to their lower distribution coefficients in HNO_3 [3, 4, 6]. Elution chromatograms of Ca, Sr and Ba obtained in this laboratory indicated that the larger part of Ca and a portion of Sr were eluted by the treatment with 2 mol/l HCl, but the total amount of Ba was eluted with the elements to be determined. In order to evaluate the efficiency of the separation, we carried out experiments according to [4], which showed that the removing efficiency of Ba and its final concentration depended on the initial content of that element. For example, the following concentration values for the final solution were found for two selected standard reference materials with largely different Ba content (G-2, 1870 μg g^{-1}, and BHVO 135 μg g^{-1}): 7–9 μg ml^{-1} according to procedure [4] and 17–19 μg ml^{-1} (this method) for G-2, and 2–4 μg ml^{-1} and 6–8 μg ml^{-1}, respectively, for BHVO. For that reason it seemed more reasonable to verify the interference effect of these elements in the maximum concentrations found according to the latter method in the final solution. Therefore, we measured synthetic mixtures of Hf, Sc and Y and one of the alkaline earth elements Ca, Sr and Ba and a combination of these elements. The following concentrations were used: Hf 1 μg ml^{-1}, Sc 1 μg ml^{-1}, Y 2 μg ml^{-1} and Ca 50 μg ml^{-1}, Sr 20 μg ml^{-1} and Ba 50 μg ml^{-1}. The values obtained were statistically treated. Comparison between different series of measurements (n = 5) using Student's criterion showed that the tabular value 2.02 for t(4,4) P = 0.1 is above those found (t_{exp}), which, for the series in the presence of the three elements were t(Hf) = 1.92, t(Sc) = 1.98 and t(Y) = 1.38. This means that for the above concentration values Ca, Sr and Ba do not affect the determination of Hf, Sc and Y. This fact has also been mentioned by [6], but no concentration values were reported. Results obtained by our method with a few geochemical reference materials are presented in Table 1. The precision values presented in terms of standard deviations, were obtained from

Table 1 Determination of Hf, Sc and Y in reference materials (results in μg g^{-1})

Samples	Number of analysis (n)	Elements	This work	Ref [4]	Ref [11]	Ref [12][a]
AGV-1	3	Hf	4.9 ± 0.7	5.2	5.45	*5.1*
		Sc	11.4 ± 0.5	12.4	11.4	*12.2*
		Y	16.6 ± 0.9	17.5	17.2	*20*
G-2	5	Hf	6.9 ± 0.3	7.2	8.38	*7.9*
		Sc	3.7 ± 0.4	3.5	2.58	*3.5*
		Y	8.9 ± 0.5	8.8	8.46	*11*
W-2	3	Hf	2.3 ± 0.1	3.1		*2.56*
		Sc	33.4 ± 0.8	36.5		*35*
		Y	18.4 ± 0.1	20		*24*
NIM-G	3	Hf	11.7 ± 0.7	12.1		12
		Sc	0.8 ± 0.2.	0.9		1
		Y	128.0 ± 9.0	123		143
MAG	3	Hf	3.4 ± 0.6		3.88	*3.7*
		Sc	17.9 ± 1.1		14.3	*17.2*
		Y	25.3 ± 1.3		23.3	*28*
BHVO-1	5	Hf	4.0 ± 0.6	4.4	4.79	*4.38*
		Sc	28.9 ± 0.6	33.3	28.9	*31.8*
		Y	23.9 ± 1.0	24.5	23.6	*27.6*

[a] The values in italics are certified

several (3–6) separate analyses of reference materials. The accuracy was studied using standard reference materials. The values obtained coincide well with the reference values [12] and with the results obtained by ICP–AES [4, 7] with lower values for Y [12]. The detection limits for these elements using the described procedure are: Hf 0.34 μg ml^{-1}, Sc 0.15 μg ml^{-1} and Y 0.42 μg ml^{-1}.

Our attempt to determine Th by the same procedure were unsuccessful. This element is very strongly retained by the resin because its distribution coefficient is very high [13]. Under the elution conditions it can not be eluted simultaneously. Experiments with increased concentration of oxalic acid and amount of eluent [14] did not yield satisfactory results.

Conclusion

A method for the determination of Hf, Sc and Y in geological materials after matrix separation with 2 mol/l HCl has been described. It does not need a supplementary elution of the major matrix elements with HNO_3 to completely eliminate Ca, Sr, and Ba, because their final concentrations do not disturb the ICP–AES measurement

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